

Journal of General Chemistry
(U.S.S.R.) 8, 524-8 (1958)
Pa 1750

NITROSYL BOROFLUORIDE AND ITS USE IN THE FLUORINATION

Voznesenskii, S. A. and Kirakii, P. P.

Wilke-Dorfurt and Balz⁽¹⁾ obtained NOBF₄ in 1927. In 1954 Balz and Mailänder⁽²⁾ considerably improved the original method of preparation of nitrosyl fluoborate. The improved method consists essentially of passing gaseous N₂O₃ into a concentrated aqueous fluoboric acid, according to the following reversible reaction:



The resulting precipitate is filtered and dried and may be further purified by distilling in vacuo. The purified product appears as colorless, hard crystals.

On warming with potassium fluoride, nitrosyl fluoborate is decomposed yielding nitrosyl fluoride and potassium fluoborate, as shown in the equation:



Thus, from the chemical point of view, the nitrosyl fluoborate possesses both the properties of nitrous acid and the fluoboric acid. It was therefore logical to expect that nitrosyl fluoborate can be used as a raw material for preparation of diazonium fluoborates, as shown in the following equation:



As it is known, Schiemann⁽³⁾, used the following method in his preparation of diazonium fluoborates:



These diazonium fluoborates are to be considered as convenient intermediates for obtaining aromatic fluoride derivatives



The purpose of this work was to study the reaction of aniline with nitrosyl fluoborate. Preliminary investigations concerned themselves with development of a new and more economical method of preparation of nitrosyl fluoborate

PREPARATION AND PROPERTIES OF NITROSYL FLUOBORATE

Preparation of nitrosyl fluoborate was carried out utilizing the interaction of nitrogen dioxide (NO₂) and fluoboric acid. The oxide of nitrogen was prepared by action of nitric acid on copper turnings. On cooling the oxide was obtained as a liquid and was thus collected and stored in small glass bulbs. The liquid N₂O₃ obtained in this manner was green colored, showing it to be contaminated with H₂O₂. In order to obtain chemically pure N₂O₃, the authors mixed the crude N₂O₃ with a small amount of concentrated HNO₃ and phosphoric anhydride (phosphorus pentoxide). It was then distilled through tubes filled with CaCl₂ and P₂O₅. Preparation of strong fluoboric acid solution was carried out by the method of

2

Rajz (2). In the tests reported in this study fluoroboric acid solutions containing 0.6 grams HBF_4 in 1.0 ml of solution were used. In order to characterize the reaction between nitrogen dioxide and fluoroboric acid solutions, the authors studied the kinetics of absorption of NO_2 by HBF_4 at two different temperatures.

The high degree of reactivity of NO_2 , in particular towards mercury, has forced the authors to discard the usual methods employed in the studies of absorption of gases by liquids. The following apparatus and procedure, adapted after numerous preliminary tests, are shown in Figure 1.

Figure 1. Apparatus for the study of the reaction of NO_2 with HBF_4 .

The reaction vessel A consists of two cylinders attached to each other by means of a ground glass joint. One cylinder has a feed tube fitted with a valve (1) and an aperture in the ground glass joint. The other cylinder has an opening in the ground glass joint, and is fitted with a shallow vessel g such a manner that rotation of the ground glass joint may either connect the cylinder g or disconnect it. The cylinder A is then connected by means of a tube to a surge cylinder C fitted with a tee joint with two valves. One valve (2) is open to the atmosphere, the other one (3) is connected through an anhydrous calcium chloride tube to a gas burette D. The gas burette D is connected by means of a syphon L to a pan (shallow vessel) K, filled with water.

Each test was carried out as follows: small cylindrical vessel (g) was filled with a strong solution of fluoroboric acid (containing 0.6 grams of HBF_4 in 1 ml of solution). Total volume of HBF_4 - 10 ml. The absorbing surface of solution - 0.64 cm^2 . With valves (1) and (2) open and valve (3) closed and the aperture to vessel g closed by means of the ground glass joint, the system (cylinder A and surge vessel C) were filled with NO_2 gas. Valves (1) and (2) were then closed and valve (3) was open. The ground glass joint was then rotated in order to connect vessel g with cylinder A, thus bringing NO_2 in contact with HBF_4 . At the instant of connecting the two cylindrical vessels, the stop watch was started and the time count begun on the volume of water sucked into the gas burette from the shallow vessel K by means of syphon L. The rate of filling of burette D with water thus corresponded to the rate of absorption of NO_2 in the HBF_4 solution. In the manner the rate of absorption of NO_2 in the HBF_4 solution was obtained at two temperatures - 25 and 40°C and for comparison the rate of

- 3 -

absorption of NO_2 in water was obtained at 25°C . Repeated tests under indicated conditions gave easily reproducible results. It must be pointed out, however, that the above described method is not an absolute one: first, the absorption data may only be obtained during a relatively short time interval (less than one hour), since in longer tests the NO_2 gas phase starts diffusing through the CaCl_2 tube into the gas burette D, thus producing erroneous results; second, with sufficiently high absorption rates the erroneous data are obtained due to capillary action of syphon tube L (the water flow through syphon L was found to be insufficient for high absorption rates). For the above mentioned reasons the data obtained pertaining to absorption of NO_2 by HBF_4 solutions and by pure water are only relative and qualitative. The results of these tests are listed in Table 1 and are plotted in figure 2 (curve 1 is for H_2O , 2 and 3 are for HBF_4). Absorption of NO_2 is shown in ml per 1 cm^2 of absorbing surface. As shown in table 1, the rate of absorption of NO_2 by HBF_4 at 25°C is considerably less than by water and it decreases with the rise in temperature.

Table No. 1

Time (min.) from start of test	Absorption by HBF_4		Absorption by water at 25°C
	at 25°C	at 40°C	
1	12.7	6.2	54.1
2	21.1	13.4	94.0
3	29.5	19.5	126.2
4	34.9	23.0	146.0
5	40.0	24.7	160.7
6	43.7	25.8	168.5
7	46.3	26.6	170.7
8	47.5	27.2	161.5
9	-	-	165
10	51.3	27.8	168.6
12	53.5	-	190.7
14	55.6	29.2	192.2
16	56.8	-	195.4
20	60.6	31.0	195.7
25	65.2	33.8	198.4
35	72.2	37.0	202.0
50	771.1	45.2	209.6

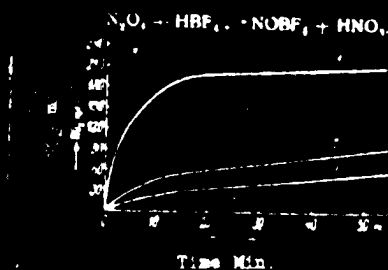


Table No. 2

Sample Weight Grams	Weight (grams) of resultant KBF ₄	KBF ₄ percent of Theoretical
0.9956	0.9994	100.30
1.0440	1.0512	100.69

Table No. 3

Sample weight Grams	Percent Nitrogen in Sample	
	Found	Theoretical
0.6455	11.98	11.95
0.4842	12.11	-

Preparations of nitrosyl fluoborate from H_2O_4 and HBF_4 were carried out: the H_2O_4 gas was bubbled slowly through the glass cylinder A, partially filled with the strong HBF_4 solution until the resultant reaction mass formed a jelly-like consistency from the precipitated NOBF_4 , according to the reaction:



The colorless and transparent mass of NOBF_4 crystals was filtered off on the asbestos filter, the filtrate was concentrated by evaporation and then further treated with H_2O_4 . After the second crop was obtained by filtration, the filtrate was again concentrated by evaporation, treated with H_2O_4 and again filtered. Total yield of NOBF_4 was 90-92 percent of theoretical.

Comparing the yield data obtained by the authors from preparation of nitrosyl fluoborate from H_2O_4 and NBF_4 with the data of Bais⁽²⁾, who used H_2O_2 and HBF_4 to prepare the nitrosyl fluoborate, it is possible to conclude that in nitric acid the equilibrium of the reaction is shifted more to the right than it is in water.

The nitrosyl fluoborate product was dried under vacuum over P_2O_5 for two days and then was further purified by vacuum distillation at 2mm Hg and 250°C.

The product was then analyzed for BF_4^- and for nitrogen. The BF_4^- was determined as KBF_4 , which is only very slightly soluble in water (at 20°C 1 gm KBF_4 in 225 and H_2O). The nitrogen content of the nitrosyl fluoborate product was determined by the Devarda method. These data are listed in tables 2 and 3.

Nitrosyl fluoride is hydrolyzed in water according to the following equation:



It reacts with bases and with alkali chlorides:

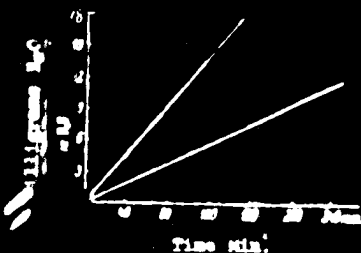
- 5 -



Nitrosyl fluoborate is very hygroscopic. The authors studied kinetics of sorption of water vapor by the method described by McBain (4). The data obtained are listed in table 4 and are plotted in figure 3.

Table No. 4

Temperature 20°C., Water Vapor Tension 16.3 mm		Sample Weight 0.0200 Grams Water Vapor Tension 16.2 mm	
Time (min.) after start of test	Absorption in grams	Time (min.) after start of test	Absorption in grams
2	0.0002	2	0.0003
6	0.0003	4	0.0007
10	0.0006	6	0.0009
15	0.0008	8	0.0011
30	0.0015	10	0.0015
45	0.0022	15	0.0020
60	0.0031	20	0.0025
90	0.0047	30	0.0032
120	0.0060	30	0.0037
180	0.0087	60	0.0050
240	0.0125	180	0.0125



Use of nitrosyl fluoborate in fluorination reactions: As mentioned in the introduction, it is possible to carry out fluorination of aromatic materials with the help of nitrosyl fluoborate, as shown in the following scheme:



In this scheme the only reaction that has not been extensively studied is the conversion of aniline to the diazonium fluoborate. Interaction of aniline and crystalline nitrosyl fluoborate leads to formation of tarry mixtures which in turn rather rapidly setup as a thick black mass (a mess!)

- 6 -

The aqueous alcohol solutions of aniline produce with NOBF_4 a precipitate of $\text{C}_6\text{H}_5\text{N}_2\text{BF}_4$; however, the yield and the purity of product are low due to formation of tarry by-products and residues.

Preparation of phenyldiazonium fluoroborate is conveniently and rapidly carried out with up to 90 percent yields if an alcohol solution of aniline hydrochloride is treated with a small excess - about ten percent - of crystalline nitrosyl fluoroborate in the $3-5^\circ\text{C}$ temperature range, which is achieved in carrying out the reaction in an ice bath. The optimum composition of the reaction mass was established to be as follows: one part aniline hydrochloride, 5.5 parts water, 4.0 parts ethyl alcohol and 1.4 parts of nitrosyl fluoroborate (by weight). The reaction product is obtained in a relatively pure state as needle-like crystals, pale rose in color, having all of the chemical and physical properties attributable to $\text{C}_6\text{H}_5\text{N}_2\text{BF}_4$, as already described in the literature. Thermal decomposition of the above mentioned phenyldiazonium fluoroborate product, as described by Schumann (5), yields theoretical quantity of fluorobenzene, melting point 85°C , freezing point -40.8°C .

CONCLUSIONS

1. Preparation of nitrosyl fluoroborate by the action of nitrogen dioxide on aqueous fluoroboric acid was studied in detail. The rate of absorption of water vapor by crystalline nitrosyl fluoroborate was determined.
2. Preparation of phenyldiazonium fluoroborate by the interaction of nitrosyl fluoroborate and aniline (as hydrochloride) was also studied. Optimum condition for the reaction were established.

LITERATURE

1. Wille-Dorffurt and Balz. Z. allg. anorg. Ch., 151, 219 (1927)
2. Balz and Mailander, Z. allg. anorg. Ch., 217, 161 (1934)
3. Schumann, G., J. prakt. Ch., 140, 97 (1934)
4. McBain, Lucas and Chapman, J. Am. Soc., 52, 2668 (1930)

Translation by:
V.V. Levasheff
5/14/58
ems